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NANOCOMPOSITES FOR SOLDIER BALLISTIC PROTECTION

WORKSHOP PROCEEDINGS

by
Michael Sennett
and
Thomas Tassinari

October 1999

Final Report
12-13 April 1999

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U.S. Army Soldier and Biological Chemical Command
Soldier Systems Center
Natick, Massachusetts 01760-5020

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
October 1999	Final	12-13 April 1999

4. TITLE AND SUBTITLE
Nanocomposites for Soldier Ballistic Protection
Workshop Proceedings

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Michael Sennett
Thomas Tassinari

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
907MFH

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Soldier & Biological Chemical Command
Soldier Systems Center, Materials Science Team
AMSSB-RSS-M
Natick, MA 01760-5020

8. PERFORMING ORGANIZATION REPORT NUMBER
NATICK/TR-00/002

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

A workshop on Nanocomposites for Soldier Ballistic Protection was conducted on April 12-13, 1999 at the US Army Soldier Systems Center, Natick, MA. Researchers and planners from academia, industry and government participated in brainstorming sessions to discuss the potential of nanotechnology to contribute to the development of materials for improved personnel armor. The discussions identified challenges that need to be addressed and opportunities that exist to exploit nanocomposites for armor applications.

15. SUBJECT TERMS
NANOTECHNOLOGY BALLISTIC PROTECTION BODY ARMOR COMPOSITES MATERIALS ARMY PERSONNEL PERSONNEL ARMOR NANOCOMPOSITE WORKSHOPS

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
U	U	U	SAR	23	Michael Sennett
					19b. TELEPHONE NUMBER *(Include area code)* (508) 233-5516

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Preface and Acknowledgements

The opinions, predictions or conclusions expressed herein are not the official policy of the Department of the Army and should not be so construed. The descriptions of research and development needs and opportunities herein are not to be construed as a commitment by the Natick Soldier Center (NSC) or any agency of the United States Government to provide funds for any specific research programs. This document is not a request for proposal (RFP) or other official instrument of the federal acquisition process.

The authors wish to thank all the attendees of the Nanocomposites for Soldier Ballistic Protection Workshop for their contributions to the discussions that led to the production of this document. Thanks to Janet Ward of NSC and Gary Hagnauer of the Army Research Laboratory, Aberdeen, MD, for their presentations and contributions they made as members of the Planning Committee for the Workshop. Thanks also go to Nora Beck Tan and Robert Dowding of ARL and to JoAnn Ratto, Cheryl Stewardson and Stephen Fossey of NSC for their work as facilitators. The authors also express their appreciation to Dee Dench, Deborah Cobban and Charlene Slamin of NSC for administrative and logistics assistance.

NANOCOMPOSITES FOR SOLDIER BALLISTIC PROTECTION
WORKSHOP PROCEEDINGS

I. Introduction

A workshop entitled "Nanocomposites for Soldier Ballistic Protection" was held at the Soldier Systems Center, Natick, Massachusetts, on April 12th, 1999 to discuss the potential role nanotechnology, and specifically nanocomposite materials, could play in the development of new ballistic protection materials for the warfighter. Fifty scientists specializing in nanomaterials research and representing industry, academia and government organizations attended. This report summarizes the discussions and conclusions arising from this workshop and from the subsequent meeting of government representatives on April 13th, 1999.

II. Background

Recent technical reports of the fabrication of composite materials, in which one of the phase domains is on the order of a few tens of nanometers in size, have attracted a great deal of attention in the materials science community (1-7). These materials exhibit significantly enhanced properties relative to composites with the same chemical composition, but in which the phase domains are larger than nanometer scale. Significantly, the enhanced properties observed in the nanocomposites do not have to come at the expense of other properties as is often observed when adding reinforcing fillers to a material. For instance, it is common to experience a loss of fracture toughness as the modulus is increased when micron-sized hard-particle reinforcement is added to a polymer. Nanometer scale reinforcements, in contrast, have demonstrated the ability to provide across the board enhancement of composite properties. The nanocomposites have also been shown to exhibit properties significantly different from the raw materials from which they are fabricated, such as conductivity, improved flame resistance or reduced gas permeability (4,8).

Due to the demonstrated potential of nanocomposites for use in a wide variety of applications, a great deal of research has been undertaken to elucidate the origin of nanocomposite properties and to develop new materials of this type. One area of potential application for

nanocomposites that has not been investigated to date is the use of these materials for ballistic protection. In general, the ultra-high or ballistic strain rate properties of nanomaterials, and particularly nanocomposite materials, have not been studied.

The current ballistic protection equipment, or body armor, that a soldier carries can weigh 18 pounds or more, depending on the specific ballistic threat being defended against. This is a very significant proportion of the soldier's overall load, and it is for this reason that current research and development efforts aimed at lightening the load of the individual warfighter give particular consideration to this part of the soldier system.

In light of the early observations of enhanced mechanical properties in nanocomposites, the Natick Soldier Center's (NSC) Material Science Team has initiated a program to investigate the ballistic response of nanocomposite materials. This study is intended to determine the near-term potential for nanocomposites to play a role in the development of materials for use in ballistic protection systems with reduced weight relative to current designs. Additional study of new armor material concepts, including materials nanotechnology, are being undertaken by the Army Research Laboratory within the framework of the Army's Strategic Research Objective (SRO) "Armor Materials by Design."

III. Workshop Objectives

The overarching objective of the workshop was to try to answer the question, "What role can nanotechnology play in the development of new materials for soldier ballistic protection?" The intention was to focus on the single issue of ballistic protection out of the wide range of potential applications of nanomaterials because this is one of the highest priority elements of the NSC mission and an Army SRO thrust. In this context an extensive technical discussion was conducted in which a wide range of issues was treated, from definition of the term "nanocomposite" to practical considerations for the safe use and handling of nanoparticulate raw materials.

Additional objectives of the workshop included information exchange and program planning. Representatives

of the Natick Soldier Center and the Army Research Laboratory (ARL) presented information on current body armor materials as well as concepts and current research on improved armor materials. Some of this work is being conducted under the auspices of the NSC with Defense Advanced Research Project Agency (DARPA) support and through the Multi-disciplinary University Research Initiative (MURI) program administered by ARL/ARO. During the workshop discussions, academic and industrial representatives reported some of the most recent developments in the nanomaterials field. Finally, the government representatives convened in a closed session the following day to discuss current and future research plans.

IV. Overview of Presentations by Army Representatives

Gary Hagnauer, Senior Scientist (ST) of the Army Research Laboratory, Aberdeen MD, presented an overview of the Army research plan for armor materials. This plan is embodied in a Strategic Research Objective (SRO) entitled "Armor Materials by Design." The long-range technical objectives of the SRO are as follows:

- Advanced armor designs that integrate ballistic, blast, NBC, EM and flammability protection with the stealth, power, sensor, computing, communications, and structural requirements of future Army systems
- Novel, lightweight, integrated and multifunctional materials/structures that significantly enhance survivability, are affordable, and sufficiently versatile to serve a wide range of system needs
- Ultra-lightweight personnel armor that provides broad spectrum threat protection against fragmenting munitions, flechettes, bullets and blast
- Advanced methods for the control and management of all military signatures including those of optical, EM and acoustic origin

Janet Ward, Ballistics Team Leader at the Natick Soldier Center, made a presentation on the NSC program in personnel armor. Examples of current personnel armor were exhibited to the workshop attendees. Key personnel armor requirements being addressed by the R&D effort at NSC include:

- Increased penetration resistance and resistance to multiple threats, with less weight and bulk
- Protection from blast and blast overpressure (shock wave)
- Cost reduction
- Producibility
- Comfort
- Durability

Technical barriers and challenges identified in the presentation are:

- Understanding complex interactions of material components in the time frame of ballistic events over a broad spectrum of ballistic threats
- Development and integration of high performance materials into ballistic protection systems
- Reduction of weight and bulk associated with increased levels of protection
- Understanding the coupled response of the human body and armor system at high strain rates against a spectrum of threats
- Defining a minimum set of test protocols independent of the material system to simulate extremes in service conditions with the potential to degrade ballistic protection

V. Overview of the Workshop Discussions

If a consensus was reached on the applicability of nanocomposites to advanced personnel armor, it was that while a definitive judgement cannot be made at this time, there is sufficient evidence to believe that these materials have good potential for this application. The evidence cited was the reports published to date indicating the large performance gains for certain matrix-nanofiller couples, relative to the parent matrix materials. Additional evidence is that nanocomposites have been shown to exhibit "non rule of mixtures" behavior, that is, properties of the composite can exceed those of any single component (Refs. 1-8 and refs. therein). At this time it appears that no one has evaluated the ballistic response of nanocomposite materials with phases of different composition.

One of the key facts gleaned from the discussions is that the field of nanomaterials and particularly nanocomposites research is still in its infancy. Very few nanocomposites have been produced in significant volumes and the characterization of the materials that have been prepared is generally incomplete. It was clear from the discussions that the origins of the various "nano-effects" observed to date are poorly understood. Continued investment in fundamental (6.1) research is needed to understand the origin of so-called "nano-effects" and how to design nanocomposite materials in order to control and optimize such effects. More applied research studies are needed to scale-up the synthesis and processing of nanocomposites and fabricate test specimens for structure-property evaluation.

The workshop discussions also suggested that the current state of materials modeling is not adequate to predict the properties of nanocomposites in advance of their fabrication. It was repeatedly brought out in discussion that significant additional effort is needed in order to develop models that adequately describe the influence of the nanoscale architecture on component materials properties. The large volume fraction of nanocomposites residing in the so-called interphase region between dissimilar materials (e.g., polymer matrix and nanoparticulate dispersed phases) makes accurate description of this complex interaction imperative for a successful predictive model of such materials to be realized.

VI. Observations and Recommendations

A. Definition of "nanocomposite"

The participants generally agreed that the term nanocomposite properly applies to materials with multiple phases (or heterogeneities) in which at least one such phase is smaller than 100 nm in one dimension. The 100 nm threshold is based on published evidence that non-linear changes in material properties are most often observed when dispersed phase dimensions reach this level. It was also suggested that the "nano-effect" is best observed when the ratio of dispersed phase size (the nanoscale dimension in high aspect ratio dispersed phases) to separation length

was on the order of 1:1, implying a limiting dependence of the effect on dispersed phase concentration.

B. Key attributes of nanocomposites to be exploited for specific applications

The following list of properties highlights aspects of the nanocomposite architecture that may be used to advantage in the design of materials with specific functionality, including impact resistance.

- High interfacial area per unit volume
- Large volume of interphase material with potentially unique and controllable properties
- Highly controlled architectures
- Stabilization of non-equilibrium phases (observed)
- Small spacing between heterogeneities (short diffusion pathways)
- Interesting confinement effects in continuous phases
- Non "rule of mixtures" behavior

C. Critical issues to address in research into the design and fabrication of nanocomposites

- Particle properties, including geometry
- Interphase properties
- Phase concentration (affects confinement volume)
- Dispersion
- Secondary (mesoscale) architecture
- Characterization
- Producibility

In particular, the issue of dispersion was repeatedly cited as critical to the successful preparation of nanocomposite materials with optimal properties. Achieving full (i.e. nanoscale) dispersion has been accomplished by modification of particle surface chemistry, which in turn has an effect on the interphase region. Control of the interphase was cited as often as dispersion as being crucial to controlling the properties of nanocomposites and it is clear that the issues of dispersion and interphase composition are inextricably linked.

It has not been determined what particle or interphase properties will deliver optimum material performance in a ballistic event. It is possible that hard particles will render specific advantages to the composite in the area of projectile break-up, while energy dissipation may be more effectively accomplished by other reinforcing domain compositions. Likewise, different aspects of a projectile defeat mechanism may best be served by very different interphase characteristics.

Characterization applies to numerous aspects of composite structure, perhaps most critically dispersion and interphase composition. In order for nanocomposites to be prepared with reproducible properties, these factors have to be carefully evaluated and controlled.

Producibility refers to the ability to manufacture the composites reproducibly and economically, and to be able to fabricate the materials into test samples and prototype parts on a sufficiently large scale to allow full evaluation of properties.

D. Nanocomposite materials with potential near-term availability and applicability to personnel armor.

The following nanocomposite materials were felt to be available in sufficient quantity and with adequate reproducibility as to enable meaningful testing of their response to ballistic impact. These materials were also considered to have the potential to exhibit properties useful in armor applications. This list also is indicative of research areas that are currently being pursued in government and academic laboratories, and to some extent in industry (primarily represented by small business at this workshop).

- Carbon nanotube composites
  - Polymer matrix
  - Ceramic matrix
- Nanoclay composites
  - Polymer matrix systems with montmorillonite or other high-aspect ratio (synthetic) silicate particles
- Dendrimer-containing composites
- Nanocomposite transparencies
- Polymer matrix with ceramic nanoparticles

- High density nanocomposites (metallics)
- Micro or nanolaminated materials incorporating nanocomposites (hierarchy of ordered structures)
- Gradient materials

Theoretical predictions reportedly suggest that carbon nanotube-based composites could have dramatically enhanced properties relative to conventional composite materials. One study predicts a modulus of 1.33 TPa at a density of 3.0 g/cc for one such system (9). The high aspect ratio of these particles and the potential to create nanoscale architecture with a high degree of anisotropy provide further encouragement to the pursuit of this research area.

Excellent gains in mechanical properties have been observed in polymer/nanoclay composites, but no such materials have been subjected to ballistic testing. These particles also have the potential to produce highly ordered, anisotropic structures.

Dendrimers might be used to aid dispersion of other species in composites or to introduce controlled architecture into composites.

Transparencies may be a good first application for nancomposites to armor in view of the fact that current transparent armor performance is significantly lower than opaque systems. This situation makes it easier to effect significant levels of improvement.

As nanoparticulate ceramics become increasingly available and affordable, it is possible to create a variety of new composites of these particles with polymers if the particles can be effectively dispersed in the polymer matrix. Continuing research is needed to develop low cost synthetic methods for nanoparticles, methods to compatibilize particles with various matrices, characterization methods for nanoparticle structures and surface properties, and the development of nanoparticles with controlled geometry.

High-density metallic nanocomposites, originally developed for penetrator applications may have applicability as a hard layer in laminated or gradient armor designs.

The introduction of multiple levels of order or anisotropy in composite systems through laminating techniques is considered a promising method of creating energy-absorbing structures.

The production of materials with compositional gradients was considered to be both achievable in the near term (using such techniques as spin- or tape-casting) and of potential benefit in the development of armor materials.

E. Barriers to development of new armor materials

These issues pertain not only to nanocomposite materials but also to all materials considered for armor applications.

- Lack of predictive test methods for ballistic response
- No universal figures of merit for armor materials properties (hardness, fracture energy, modulus, etc.)
- Tendency of ballistic response to be sensitive to projectile composition and design (multi-body problem)
- Cost and availability of new materials
- Processing technology to fabricate components with new materials

It is generally not possible to predict high strain rate (ballistic) properties of materials from static or low strain rate test results. It would be extremely desirable to have an instrumental test method that accurately predicts ballistic response. One significant barrier to the development of such a test is that ballistic response of an armor material is sensitive to the composition and design of the projectile. It is possible to optimize an armor for a specific projectile and then find that it performs poorly against other, nominally lesser, projectile threats.

In keeping with the poor correlation between low and ultra-high rate test results, there is also no universal figure of merit for composite armor materials. An example cited at the workshop is the case of boron carbide, which has been studied as a component of composite armor systems. Boron carbide has lower fracture toughness than other armor

ceramics that it outperforms in ballistic testing. However, other similarly brittle materials do not perform well in ballistic tests. This type of anomaly frustrates attempts to develop a profile of a successful composite armor material based on physical properties.

F. Key research areas

The workshop discussions brought up areas of research where the attendees felt that additional resources could be effectively employed. Research areas that were repeatedly mentioned are listed below.

- Modeling
- Characterization
- Processing
- New materials

Echoing a theme common to many discussions of needs in the materials research community recently, the attendees frequently cited the desirability of having good predictive models for composite material properties. The crux of the problem is the need to account for the contribution of molecular level effects to the interaction of dispersed and continuous phases. The nature of this interaction has been shown experimentally to play a large part in overall composite materials properties (8). Thus, in order to have a predictive model for composite properties, the model must first predict interphase properties and then use these results to predict larger scale material behavior.

Due to the very small length scales involved in nanocomposite structures, advanced characterization methods are needed to probe the smallest features of composite architecture. Details such as particle bulk and surface composition and morphology are important to study. Determining the degree of dispersion of nanoparticles in various matrices is a critical issue. Finally, characterization of the particle-matrix interphase in terms of size, composition and mechanical properties is of great importance to the study of nanocomposites.

The development of new and improved processing techniques for synthesizing and fabricating nanocomposites is needed. One of the main factors limiting the characterization of nanocomposites as structural materials, particularly for ballistic response, is the relative

scarcity of these materials, or the inability to fabricate samples larger than a few cubic centimeters. A key area of process control, being addressed by a number of researchers, is that of nanoparticle dispersion and compatibilization. Without full dispersion to the level of the primary particle, it is unlikely that the full potential of any given filler/matrix couple will be realized. An additional promising area of research is the development of self-assembly mechanisms to create specialized materials architecture. Finally, processing composites into large-scale forms such as structural components for systems applications (such as armor) needs to be pursued for nanocomposite materials. It is necessary to take nanocomposite raw materials and fabricate them into large-scale test specimens and prototype parts. This can be difficult for polymer matrix composites using traditional processing methods such as extrusion or injection molding in that the inclusion of nanoparticles, particularly high-aspect ratio particles, in polymer systems can lead to large viscosity increases. Alternative processing methods or modification to existing processing methods are needed to allow fabrication of large-scale nanocomposite forms and also to preserve and maximize the potential of the nanocomposite architecture.

VII. The NSC Nanomaterials Program Future Directions and Priorities.

The immediate focus of the NSC nanomaterials program will be research directed toward answering the question posed earlier in this document: "What role can nanotechnology play in the development of new materials for soldier ballistic protection?" Although this effort will not establish the limits of what may be accomplished in this application with nanocomposites, it will help establish the ballistic performance of current nanocomposites technology, which is now unknown. This will enable NSC and the Army to focus development resources on nanomaterials technologies with the greatest potential to provide leap-ahead gains in protection levels for future generations of personnel armor systems.

The NSC nanomaterials research program will pursue and support work directed at the critical issues identified in the course of the workshop. These include:

- phase dispersion,
- domain interaction (interphase control) and
- orientation of asymmetric domains,

with a view to determining how these issues affect nanocomposite properties in general and ballistic impact response in particular. Nanomaterials development programs supported by the Natick Soldier Center will focus in the near term on materials that are:

- producible (that is, available in sufficient quantity for testing, including ballistic testing) and
- reproducible (that is, well characterized and consistent from sample to sample).
- Processability will be another important criterion in selecting specific nanomaterials technologies to pursue in the near term.

The NSC will continue to partner with academic, industrial and other government organizations to leverage expertise and resources that are being applied to nanomaterials research through a diverse set of programs originating in a variety of agencies. Coordination of the NSC program with existing programs in other organizations will be vigorously pursued in order to avoid unnecessary duplication of effort and to maximize productivity.

This document reports research undertaken at the U.S. Army Soldier and Biological Chemical Command, Soldier Systems Center, and has been assigned No. NATICK/TR- 00/002 in a series of reports approved for publication.

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XI. Appendix: List of Attendees

Name	Affiliation	Phone	E-mail
Akkara, Joseph	Natick	508-233-5260	jakkara@natick-amed02.army.mil
Auerbach, Peggy	Natick	508-233-4074	mauerbac@natick-emh2.army.mil
Balogh, Lajos	U. Michigan	734-615-0623	baloghl@umich.edu
Basel, Richard	Lebensmittel (consultant)	419-435-2774	basell@mail.bright.net
Beall, Gary	Nanospec (consultant)	847-526-8376	gwbeall@aol.com
Beck Tan, Nora	ARL	410-306-0700	nora@arl.mil
Blanas, Andreas	Natick	508-233-4187	ablanas@natick-emh2.army.mil
Cunniff, Phil	Natick	508-233-5463	pcunniff@natick-emh2.army.mil
Dowding, Robert	ARL	410-306-0824	rdowding@arl.mil
Durham, Delcie	NSF	703-306-1330	ddurham@nsf.gov
Fossey, Steve	Natick	508-233-5360	sfossey@natick-amed02.army.mil
Gassner, John	Foster-Miller Inc.	781-6844173	jgassner@fostermiller.com
Giannelis, E.	Cornell U.	607-255-9680	epg2@cornell.edu
Gonsalves, Ken	U. Conn.	860-986-6131	
Hagnauer, Gary	ARL	410-306-0710	ghagnau@arl.mil
Herbert, Jean	Natick	508-233-4405	jherbert@natick-emh2.army.mil
Hsieh, Alex	ARL	410-306-0697	ahsieh@arl.mil
Kiserow, Doug	ARO	919-549-4213	kiserow@aro-emh1.army.mil
Ko, Frank	Drexel U.	215-895-1640	fko@col.drexel.edu
Laine, Rick	U. Michigan	734-764-6803	talsdad@umich.edu
Lee, B.L.	Penn State	814-237-0597	BLL10@psu.edu
Leitch, Paul	Natick	508-233-5411	pleitch@natick-amed02.army.mil
Lewis, Robert	Natick	508-233-5645	rlewis@natick-amed02.army.mil
Morse, Daniel	UCSB	805-893-8982	d-morse@lifesci.lscf.ucsb.edu

Mullins, Bill	ARO	919-549-4286	mullinsw@aro-emh1.army.mil
Niu, Chunming	Hyperion Catalysis Int'l.	617-354-9678	cmniu@110.net
Partch, Richard	Clarkson U.	315-268-2351	partch@clarkson.edu
Piche, Joseph	Eikos, Inc.	508-528-0300	jpiche@eikos.com
Ratto, JoAnn	Natick	508-233-5315	jratto@natick-amed02.army.mil
Rivin, Don	Natick	508-233-4392	drivin@natick-emh2.army.mil
Roco, Mike	NSF	703-306-1371	mroco@nsf.gov
Roth, Roy	ARO	919-967-3435	roth@aro-emh1.army.mil
Santos, Luisa	Natick	508-233-5475	lsantos@natick-emh2.army.mil
Schamber, Don	Battelle	508-647-1972	
Sennett, Michael	Natick	508-233-5516	msennett@natick-emh2.army.mil
Siegel, Richard	RPI	518-276-6373	rwsiegel@rpi.edu
Singh, Anant	Triton Systems Inc.	978-250-4200	anant@tritonsys.com
Somasundaran, S.	Columbia U.	212-854-2926	ps24@columbia.edu
Song, John	Natick	508-233-5531	jsong@natick-emh2.army.mil
Stenhouse, Peter	Natick	508-233-4114	pstenhou@natick-emh2.army.mil
Stewardson, C.	Natick	508-233-5427	csteward@natick-emh2.army.mil
Stucky, Galen	UCSB	805-893-4872	stucky@chem.ucsb.edu
Sudarshan, T.S.	Materials Modification	703-560-1371	sudarshan@matmod.com
Tassinari, Tom	Natick	508-233-4218	ttassina@natick-emh2.army.mil
Vaia, Richard	USAF	937-255-9184	vaiara@mil.wpafb.af.mil
Ward, Janet	Natick	508-233-5462	jward@natick-emh2.army.mil
Withers, J.C.	MER Corp.	520-574-1980	jwithers@mercorp.com
Woodmansee, S.	Natick	508-233-5202	swoodman@natick-emh2.army.mil